

Modelling the fate of persistent organic pollutants in Europe: parameterisation of a gridded distribution model

Konstantinos Prevedouros^a, Matthew MacLeod^b,
Kevin C. Jones^a, Andrew J. Sweetman^{a,*}

^a*Environmental Science Department, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster LA1 4YQ, UK*

^b*Lawrence Berkeley National Laboratory, One Cyclotron Road 90R3058, Berkeley, CA 94720, USA*

Received 14 July 2003; accepted 11 August 2003

“Capsule”: *A regionalised European box model is described, parameterised and tested for Lindane.*

Abstract

A regionally segmented multimedia fate model for the European continent is described together with an illustrative steady-state case study examining the fate of γ -HCH (lindane) based on 1998 emission data. The study builds on the regionally segmented BETR North America model structure and describes the regional segmentation and parameterisation for Europe. The European continent is described by a $5^\circ \times 5^\circ$ grid, leading to 50 regions together with four perimetric boxes representing regions buffering the European environment. Each zone comprises seven compartments including; upper and lower atmosphere, soil, vegetation, fresh water and sediment and coastal water. Inter-regions flows of air and water are described, exploiting information originating from GIS databases and other georeferenced data. The model is primarily designed to describe the fate of Persistent Organic Pollutants (POPs) within the European environment by examining chemical partitioning and degradation in each region, and inter-region transport either under steady-state conditions or fully dynamically. A test case scenario is presented which examines the fate of estimated spatially resolved atmospheric emissions of lindane throughout Europe within the lower atmosphere and surface soil compartments. In accordance with the predominant wind direction in Europe, the model predicts high concentrations close to the major sources as well as towards Central and Northeast regions. Elevated soil concentrations in Scandinavian soils provide further evidence of the potential of increased scavenging by forests and subsequent accumulation by organic-rich terrestrial surfaces. Initial model predictions have revealed a factor of 5–10 underestimation of lindane concentrations in the atmosphere. This is explained by an underestimation of source strength and/or an underestimation of European background levels. The model presented can further be used to predict deposition fluxes and chemical inventories, and it can also be adapted to provide characteristic travel distances and overall environmental persistence, which can be compared with other long-range transport prediction methods.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: POPs; European distribution model; Fugacity; Steady-state; γ -HCH

1. Introduction

The fate and behaviour of persistent organic pollutants (POPs) in the environment has attracted considerable scientific and political interest, arising from concern over human exposure to these chemicals, and their discovery in areas far from source regions. The ability of certain POPs to undergo long-range atmo-

spheric transport (LRAT) has resulted in the negotiation of protocols for their reduction or elimination, to reduce the risks to regional and global environments (<http://www.unece.org/env/lrtap>). The assessment of candidate POP chemicals for future addition to these protocols is based on an assessment of a number of criteria, for example, atmospheric half life, aquatic bio-concentration and presence of chemical in remote locations. These factors are inter-linked within a multimedia environment and the interactions between processes needs to be fully understood. For example, a chemical may have a high potential for aquatic food

* Corresponding author. Tel.: +44-1524-593300; fax: +44-1524-593985.

E-mail address: a.sweetman@lancaster.ac.uk (A.J. Sweetman).

chain bioaccumulation, but if emitted to soil may remain there owing to its high affinity for soil organic matter. As a result, the development of predictive models can assist our understanding of chemical fate and behaviour in a multimedia environment. Ideally these models support the development of a thorough understanding of the release of a contaminant (both quantity and emission route), its migration pathways through the multimedia environment, the dynamics of inter-compartmental exchange and its ultimate fate. Frequently, there are gaps in the information that is available for chemicals and models are used to assess whether identified sources can account for observed contaminant levels in the environment and to identify key pathways and processes based on a knowledge of physicochemical parameters and emission estimates.

An important part of the evaluation of potential POP compounds is the assessment of their potential to undergo long-range transport from source regions. Transport in air is generally the most important mechanism, but water borne transport can be significant for some chemicals. A range of model approaches has been developed to provide an assessment of chemicals' potential for LRT. These models provide rankings of transport potential for chemicals using a characteristic distance they are likely to travel or a measure of the fraction of the global environment they are likely to affect. For example, most predictive models indicate that HCB has a very high potential for LRAT, whereas B(a)P is unlikely to be transported appreciable distances (Fellin et al., 1996). The model results for relatively well-characterised chemicals are supported by measurements/observations and expert judgement, and enable 'new' compounds examined using models to be placed in context.

Generic multimedia models are used to provide an assessment of LRT potential in a standardised environment and are useful for screening-level LRAT assessments (Bennett et al., 1998; Beyer et al., 2000; Scheringer et al., 2000). Global and/or hemispheric models have also been developed using highly simplified descriptions of environmental conditions (Van de Meent, 1993; Wania and Mackay, 1995; Scheringer et al., 2000). However, there is clearly a need to concurrently develop models with region specific parameterisation (e.g. MacLeod et al., 2001) that can be directly evaluated against environmental monitoring data, given sufficient information about contaminant sources. Region specific models provide information on chemical fate and behaviour with a more realistic description of the environment, and can also provide estimates of LRAT. Such models can include region specific deposition parameters (e.g. snow and ice scavenging), regional variations in temperature driven processes, and spatially variable descriptions of emissions and environmental compartment properties.

A regionally segmented model, BETR North America, has recently been developed for North America that describes the continent as 24 watershed-based, linked regional environments (MacLeod et al., 2001; Woodfine et al., 2001). The present study builds on the BETR North America model structure and describes a regional segmentation and parameterisation for Europe. There is considerable incentive to develop such a model for the European continent; Europe is (and has been) a major global source area of POPs and reasonably sophisticated source inventory data are available. Given the complex political and economic state of the region, there is an incentive for a model that can be used as a tool to support management decisions. This paper presents details of the adaptation and restructuring of the BETR North America model to describe the European continent, along with a preliminary case study for γ -hexachlorocyclohexane (γ -HCH or lindane). The potential use of a continental-scale model for regulatory purposes is discussed, particularly for the UNECE POPs protocol.

2. Model segmentation and parameterisation

The European continent is described in the model by a 50 cell grid ($5^\circ \times 5^\circ$), together with four perimetric boxes representing the Atlantic, Mediterranean, Eurasian and Arctic "buffer zones" around Europe that directly impact (or are impacted by) contaminant levels in the European environment. Each grid represents an area of approximately 500×500 km, with the whole grid covering an area from 38.7° N to 61.1° N latitude and -10.1° to 39.4° longitude. Fig. 1 shows the model segmentation which covers a total area of 14 million km^2 .

The selection of the spatial scale and boundaries of regions in a geographically explicit model for POPs requires balancing several factors. Owing to their semi-volatile and persistent nature, many POP chemicals have been shown to travel distances in excess of 500 km. The atmospheric half-life criterion for consideration for inclusion on the UNECE POPs protocol list is 2 days. Assuming a mean wind speed of 3 m s^{-1} , this could result in a travel distance in excess of 520 km which would facilitate exchange between neighbouring grid cells. Further, the atmospheric residence time in each grid cell is approximately 28 h, which provides sufficient time for reaction and deposition processes to occur before advection flushes the atmospheric compartment. The gridded approach was also chosen to facilitate the input of atmospheric transport data from global circulation prediction models and is consistent with our emphasis on assessing long-range atmospheric transport. For the purposes of this study data from the European Centre for Medium-Range Weather Forecasts (ECMWF) global circulation model has been used,

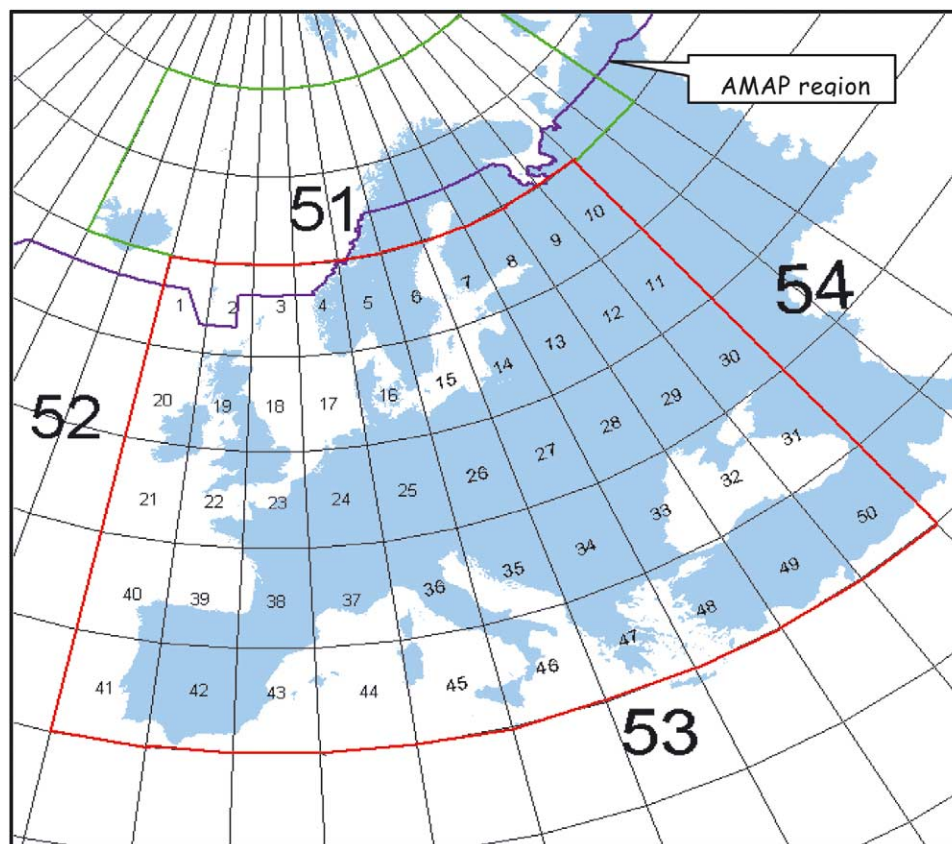


Fig. 1. Europe regional segmentation showing 50 inner cells and four perimetric zones. Area 51 represents the Arctic region.

which divides the atmosphere into a series of layers of equal atmospheric pressure and provides wind velocities, humidity and temperature on a gridded basis. The BETR North America segmentation, in comparison, is determined by water drainage basins, in order to minimise the water flow between adjacent regions (Woodfine et al., 2001).

The gridded segmentation adopted for the European model allowed the most consistent adaptation of the ECMWF data to the multimedia framework. The drawback of this approach relative to segmentation based on watershed boundaries is that parameterisation of the flow-patterns of surface water within the continent is much more difficult. Gridded segmentation still allows assessment of atmospheric deposition to surface waters, which may be of particular concern in remote areas such as parts of Scandinavia.

The bulk of the model domain (represented by the 50 grid cells) describes a surface area of 14 million km², 40% of which is covered by sea and only 1.2% by freshwater (rivers and lakes). The major sea bodies are the North, Baltic and Black Seas as well as a large part of the Mediterranean. Only 0.4% of the total land area is defined as urban. In order to transform the three-dimensional space occupied by Europe into a two-dimensional map, all landcover and environmental data was projected using a polar stereographic projection.

This starts from the North Pole and preserves the shape of its segments, creating an increasing distortion of the surface area with distance from the centre of the projection. Thus, the area of individual regions in the 5×5 degree grid range between 2 and 3 10⁵ km². In order to address the issue of the degree of spatial resolution required in continental-scale models, investigations were carried out to ascertain whether a given chemical is likely to spend enough time in each model segment to allow reactions and other processes such as deposition to occur. Assuming a constant wind speed of 3 m s⁻¹ produces an atmospheric advective residence time of around 24–48 h depending on the size of the region. This compares to vegetation deposition half times ranging from 26 to 58 h and deposition half-times to seas/coastal waters of between 22 and 38 h for γ -HCH. A higher degree of spatial resolution is therefore deemed unnecessary and will only increase the model complexity. Furthermore, it is likely that only a small fraction of the most persistent compounds emitted in Europe will react/degrade within the borders of Europe; Hexachlorobenzene, α -HCH and PCP are typical examples of such chemicals with extremely high characteristic travel distances (CTD) (Fellin et al., 1996; Wania and Mackay, 1999; Beyer et al., 2003).

The air and water flow connections between the 54 regions is specified using 54×54 spreadsheet matrices,

with a 55th region representing an area outside the model region to ensure an air mass balance. Matrices for upper and lower air, fresh and coastal water and water runoff define the flows between adjacent regions, as well as within each individual model segment. This data was gathered by exploiting information originating from Arc Info/View databases and other georeferenced data. The lower air matrix, see Fig. 2, shows the flow rates of air ($\text{m}^3 \text{h}^{-1}$) leaving region *i* and entering region *j*. The following section provides information on the parameterisation and compilation of the flow balances, together with the selected environmental datasets.

2.1. Air flow

Starting from the centre of each region, one-day forward trajectories were calculated using the British Atmospheric Data Centre ECMWF trajectory service (<http://badc.nerc.ac.uk/data/ecmwf-trj/>). The trajectories were calculated using 6-hourly operational analyses of the three components of the wind and surface pressure, which were then interpolated on to a $1.5^\circ \times 1.5^\circ$ grid. The data was linearly interpolated in time and space. The output data from the trajectories consisted of latitude, longitude and pressure of the trajectory every 30 min. Air was allowed to move freely to all other regions within the two atmospheric heights of 500 and 2000 m above sea level. The endpoints of those trajectories were then computed, producing an average wind rose for all the model segments for the period of study (1997–2001). The wind roses were then converted into a connectivity flux matrix for each atmospheric height, using a matrix technique described by Woodfine et al. (2001). Fig. 3 presents the average 5-year wind

rose of model region 19 (northwest UK), which shows the predominance of southwesterly winds.

The gridded approach to the model structure requires that the flow of fresh water through rivers is calculated at each interface between adjacent cells. This also applies to the movement of coastal water and currents in the oceans/seas. Although there is a network of gauging stations along most of the major river systems, they are of course not located at the precise intersections of the grid. Consequently, the water flow was estimated for each river system and its associated stations taking into account the proximity of the gauging station to the borderline and its elevation. Two datasets were used to quantify the water movement between adjacent regions as well as the water running off at each region's oceanic compartment (if any). Freshwater bodies were assumed to have an average depth of 20 m. The data used for the fresh water balance were extracted from:

1. A database of monthly averaged European river discharge measurements from 160 gauging stations derived from UNESCO archives. The period covered by each dataset varied from station to station. These data were checked against information obtained from the Global Runoff Centre in Kobletz (Germany) and through the US National Geophysical Data Centre in Boulder, Colorado (Vorosmarty et al., 1998).
2. The FRIEND European Water Archive Project with data from more than 5000 stations providing gauged daily flows, catchment areas and site elevations, with participation from more than 30 European countries. For the purposes of this study only stations with catchment areas greater than 5000 km^2 were selected, resulting in another

Region I

	1	2	3	4	5	6	7
1	0.00E+00	2.31E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2	6.32E+12	0.00E+00	2.31E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3	0.00E+00	5.22E+12	0.00E+00	2.06E+12	0.00E+00	0.00E+00	0.00E+00
4	0.00E+00	0.00E+00	4.18E+12	0.00E+00	1.21E+12	0.00E+00	0.00E+00
5	0.00E+00	0.00E+00	0.00E+00	9.05E+12	0.00E+00	2.19E+12	0.00E+00
6	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.33E+13	0.00E+00	1.36E+12
7	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.21E+12	0.00E+00
8	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.42E+12
9	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
11	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
13	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
14	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.10E+12
15	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.68E+12	0.00E+00
16	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
17	0.00E+00	0.00E+00	0.00E+00	7.78E+11	0.00E+00	0.00E+00	0.00E+00
18	0.00E+00	0.00E+00	2.78E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00
19	0.00E+00	2.76E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20	2.18E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Region J

Fig. 2. Part of the 54×54 lower air flow matrix-flows from region *i* to *j* $\text{m}^3 \text{h}^{-1}$.

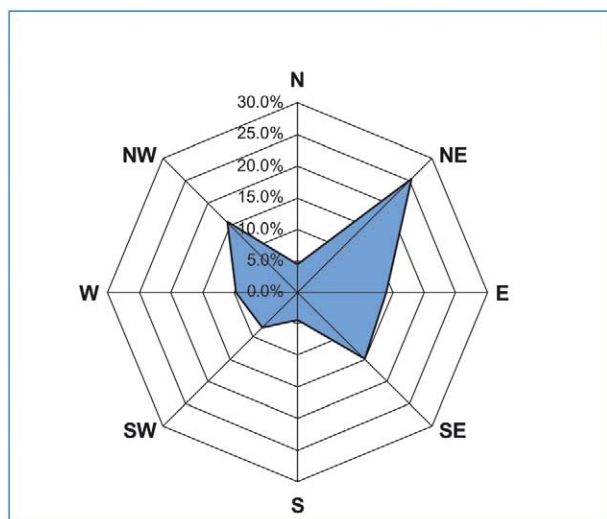


Fig. 3. Average 1997–2001 wind rose for Northwest UK.

160 stations. These data were provided by UK Centre for Ecology and Hydrology (CEH).

In order to close the water mass balance for each region an evaporation/transpiration rate was calculated for each cell using the following equation:

$$\begin{aligned} \text{Evap./Transp. rate (m}^3 \text{ year}^{-1}) \\ = \text{Net discharge (m}^3 \text{ year}^{-1}) \\ - \text{Precipitation (m}^3 \text{ year}^{-1}) \end{aligned} \quad (1)$$

where,

$$\begin{aligned} \text{Net discharge} = \text{Water outflow from a region} \\ - \text{Water inflow into the region} \end{aligned} \quad (2)$$

Fig. 4 illustrates the water balance for region 16 (Denmark) and compares riverine inputs into coastal waters, input from precipitation and coastal water residence time.

Coastal water exchange between neighbouring cells (where appropriate) has been calculated using the coastline length between adjacent oceanic regions, the average depth of each oceanic region (determined by using world bathymetry data, Smith and Sandwell, 1997) and mean current flow and direction using World Data File-Drifter data (Hansen and Poulain, 1996). An opposite flow equivalent to 10% to the dominant flow has also been included to account for seasonal changes in the movement of oceanic water.

2.2. Precipitation

Monthly averaged global climate data from the International Institute for Applied System Analyses (IIASA; Laxenburg, Austria) which includes precipita-

tion and temperature data were used in the model (Leemans and Cramer, 1991). The dataset uses standardised climate records from up to eight different sources, interpolated and smoothed to fit a one-half degree latitude/longitude terrestrial grid surface. These data were incorporated into the model by averaging the data over each grid.

2.3. Runoff water

In the context of this model this parameter refers to the volume of the water within a particular region that runs off to its own coastal water compartment per unit time. Again, the data were extracted from the two datasets used for freshwater flow calculations.

2.4. Vegetation and land cover

The land cover description of the model classifies forests, agriculture, horticulture and grassland into a single generic vegetation compartment in order to retain simplicity. The current parameterisation of the generic vegetation has been adapted from Cousins and Mackay (2001). Chemicals can be deposited onto vegetation surfaces via diffusion, wet and dry deposition, rain dissolution, as well as root uptake from soil. Runoff from the leaf surface, litterfall and volatilisation can remobilise the previously deposited chemicals. In the absence of measured data for most POP chemicals, the degradation half-life within vegetation has been assumed to be the same as in the atmosphere. However, there is some evidence that this may overestimate the importance of this loss processes.

Information on vegetation and other land features, together with the organic carbon content of European soils, was extracted from the European Land Cover map developed by the Stockholm Environment Institute, based at York University in the UK. The dataset provides geo-referenced information on 15 regions covering most of the European continent. In order to incorporate these data into the model each region had to be projected and statistically assessed to provide summary data for the 54-region model design. Land cover data for Turkey were not included in this dataset so parameterisation for regions 48–50 (see Fig. 1) was extrapolated based on the properties of neighbouring regions.

3. Model structure

MacLeod et al. (2001) and Woodfine et al. (2001) describe the compartmental structure, advective and reactive processes and regional links of the BETR North America (NA) model. The approaches used in the construction of the European model were similar. If

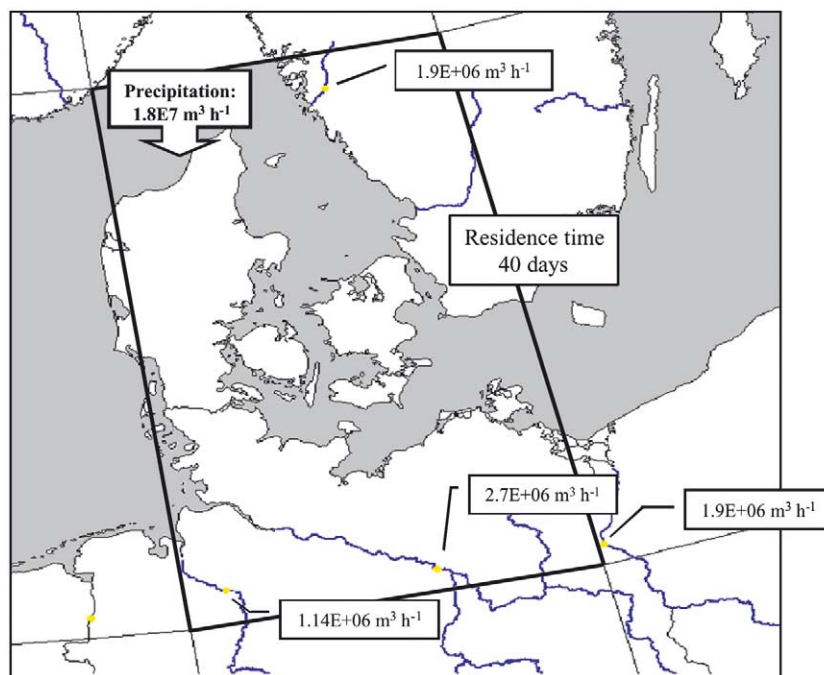


Fig. 4. Water flows for region 16.

further details of the compartmental construction are required the reader is directed to MacLeod et al. (2001) and Woodfine et al. (2001). The fate of POPs within the European model is described by seven mass balance equations for each region, resulting in 378 equations for all 54 grids. The steady state equations are summarised in Table 1, in both linear algebra and matrix algebra formats. The system of seven equations and the seven unknown fugacities can be solved analytically using either linear or matrix algebra, for which a Gauss elimination algorithm was used (MTEC, 2000). In the first iteration of the model, the analytical solutions to the steady-state regional mass balance equations yield compartmental fugacities in all regions due to local sources of contaminant only. The total emission rate to the four compartments that receive advective transfers from other regions are then calculated, and a new steady-state solution is determined. The steady-state solution for the linked set of regional models is approached by iteration until compartmental fugacity in all of the compartments does not change from its value in the previous iteration by more than 1 part in $1\text{E}+15$, which is consistent with the expected rounding error for the calculations. The linear algebra and matrix algebra solution methods yield the same solutions to a high precision, and thus serve as verification that the steady-state model is solved without errors.

The model can also be run under dynamic conditions which can be used to simulate changing emission scenarios. Historical emissions of POP compounds typically follow distinct release patterns. For example widespread production and subsequent release of PCBs

throughout the 1950s and 1960 was followed by a rapid reduction in production through the 1970/1980s. This type of emission pattern is common for many chemicals of commerce and can be simulated using the dynamic version of the model. This introduces added parameterisation and the associated uncertainties, but potentially yields a more realistic description of compound environmental fate.

The following section describes a case study which uses the steady state solution and provides an illustration of the potential use of the European model.

4. Lindane as a case study

γ -HCH or lindane was selected as a case-study chemical to test the continental atmospheric transport algorithms and to evaluate the model against available measurement data for the year of 1998. It is emphasised that this is an illustrative example of how the model might be applied to describe the continental-scale dynamics of persistent chemicals. This example uses the model's steady-state description of the processes governing the fate of lindane. A fully dynamic emission inventory coupled with dynamic model runs is likely to provide a better indication of the predictive capabilities of the model, and model calculations of this type are planned for the future. Lindane was selected for this steady-state evaluation partly due to its extensive and long-term environmental monitoring, its relatively well-documented emission estimates and its spatially confined emission sources. It is also included on the

Table 1
Model mass balance equations

Steady-state mass balance equations

(1) Upper air $f(1) \text{ DT}(1) = E(1) + f(2) \text{ D}(2,1)$

(2) Lower air $f(2) \text{ DT}(2) = E(2) + f(1) \text{ D}(2,1) + f(3) \text{ D}(3,2) + f(4) \text{ D}(4,2) + f(5) \text{ D}(5,2) + f(6) \text{ D}(6,2)$

(3) Vegetarian $f(3) \text{ DT}(3) = E(3) + f(1) \text{ D}(1,3) + f(2) \text{ D}(2,3) + f(6) \text{ D}(6,3)$

(4) Fresh water $f(4) \text{ DT}(4) = E(4) + f(1) \text{ D}(1,4) + f(2) \text{ D}(2,4) + f(6) \text{ D}(6,4) + f(7) \text{ D}(7,4)$

(5) Coastal water $f(5) \text{ DT}(5) = E(5) + f(1) \text{ D}(1,5) + s(2) \text{ D}(2,5) + f(4) \text{ D}(4,5)$

(6) Soil $f(6) \text{ DT}(6) = E(6) + f(1) \text{ D}(1,6) + f(2) \text{ D}(2,6) + f(3) \text{ D}(3,6)$

(7) Sediment $f(7) \text{ DT}(7) = E(7) + f(4) \text{ D}(4,7)$

Matrix algebra format

$f(1)$	$f(2)$	$f(3)$	$f(4)$	$f(5)$	$f(6)$	$f(7)$	RHS
$\text{DT}(1)$	$-\text{D}(2,1)$	$-\text{D}(3,1)$	$-\text{D}(4,1)$	$-\text{D}(5,1)$	$-\text{D}(6,1)$	$-\text{D}(7,1)$	$E(1)$
$-\text{D}(1,2)$	$\text{DT}(2)$	$-\text{D}(3,2)$	$-\text{D}(4,2)$	$-\text{D}(5,2)$	$-\text{D}(6,2)$	$-\text{D}(7,2)$	$E(2)$
$-\text{D}(1,3)$	$-\text{D}(2,3)$	$\text{DT}(3)$	$-\text{D}(4,3)$	$-\text{D}(5,3)$	$-\text{D}(6,3)$	$-\text{D}(7,3)$	$E(3)$
$-\text{D}(1,4)$	$-\text{D}(2,4)$	$-\text{D}(3,4)$	$\text{DT}(4)$	$-\text{D}(5,4)$	$-\text{D}(6,4)$	$-\text{D}(7,4)$	$E(4)$
$-\text{D}(1,5)$	$-\text{D}(2,5)$	$-\text{D}(3,5)$	$-\text{D}(4,5)$	$\text{DT}(5)$	$-\text{D}(6,5)$	$-\text{D}(7,5)$	$E(5)$
$-\text{D}(1,6)$	$-\text{D}(2,6)$	$-\text{D}(3,6)$	$-\text{D}(4,6)$	$-\text{D}(5,6)$	$\text{DT}(6)$	$-\text{D}(7,6)$	$E(6)$
$-\text{D}(1,7)$	$-\text{D}(2,7)$	$-\text{D}(3,7)$	$-\text{D}(4,7)$	$-\text{D}(5,7)$	$-\text{D}(6,7)$	$\text{DT}(7)$	$E(7)$

$f(x)$, fugacity of chemical in compartment x , Pa; $E(x)$, emission rate to compartment x , mol/h; $V(x)$, volume of compartment x , m^3 ; and $Z(x)$, fugacity capacity of compartment x , $\text{mol}/\text{m}^3 \cong \text{Pa}$.

UNECE POPs protocol list of chemicals that are considered to undergo LRAT and exhibit high overall environmental persistence, based on measurement data documenting its ubiquity in the environment.

Lindane has been extensively used worldwide as an agricultural insecticide (Li et al., 1998), with most of the European countries having banned or severely restricted its use since the mid-1990s. European estimates suggest that as much as 135,000 tonnes was applied over the period 1970–1996 (Breivik et al., 1999); with the major emissions originating from France, Spain and the Netherlands. Breivik and co-workers estimated that approximately 650 tonnes/year were still being emitted in 1998 and have also calculated the contribution of each European country. For the purposes of this illustration, lindane emission estimates for 1998 have been used and integrated into the model's regional structure, as presented in Fig. 5. For the purposes of this initial evaluation of the performance of the model, all emissions were assumed to be to the lower atmosphere compartment of the model.

In addition to the direct application of lindane there may also have been diffuse emission sources such as from disused chemical factories or/and emissions from dumps (Manz et al., 2001) revolatilisation from soils and other lindane-treated surfaces, as well as significant amounts “imported” into the European environment from the West and East. For this reason, two types of model runs have been considered. The first assumes no

background lindane concentration in any of the environmental compartments under consideration. In this way, the atmospheric transport of the selected chemical can be tested under the current model parameterisation. The second evaluated scenario applies an estimated background concentration to simulate advection into Europe. The ambient air levels can, thus, be supported and the predicted spatial distribution of atmospheric lindane concentrations may better resemble the distribution obtained by various sampling campaigns. Steady-state concentrations for both scenarios in air and other environmental media have been predicted and compared to measured data from the same time period (1998). As a result, both the validity of the existing emission inventories (inherently uncertain in nature) and, to a lesser degree, the performance of the model can be tested. Furthermore, compartmental distributions, deposition fluxes and chemical inventories have been predicted. The model can also be adapted to provide CTDs and overall environmental persistence of γ -HCH, which can then be compared to other LRAT-predictive models. It should be emphasised that the model described herein is only at its initial testing stage and results should be treated with caution. In addition, while the model predicts average regional lindane concentrations monitoring data from only one station in some of the segments was taken into account, making direct comparisons between the model and data difficult.

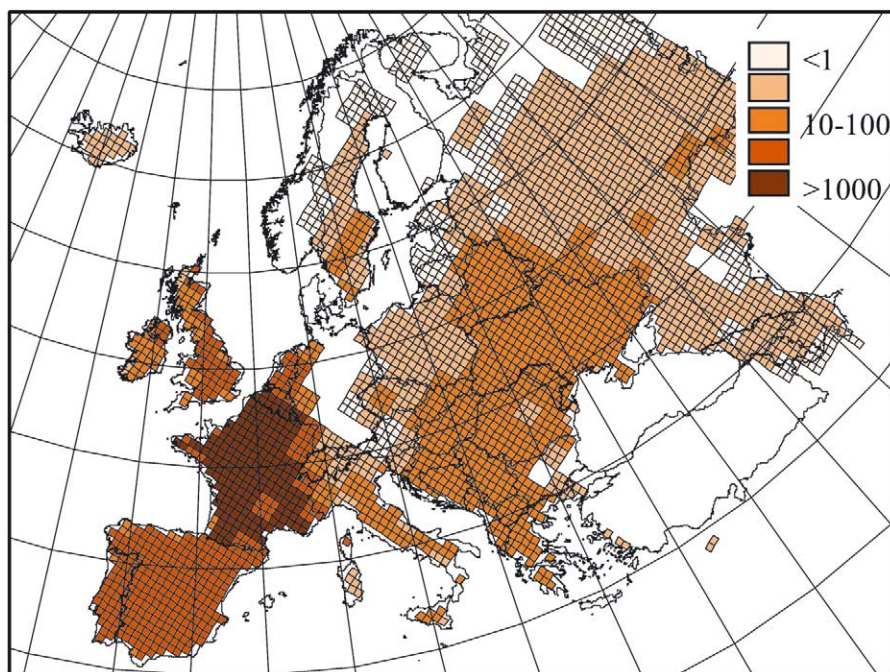


Fig. 5. 1998 lindane emissions (kg).

5. Case study results and discussion

Predicted steady-state concentrations for each of the seven environmental compartments were calculated, with the lindane distribution in the lower air and soil compartments presented in Fig. 6a and b. Fig. 6a reveals, as expected, that the highest lower-air concentrations are the ones closest to the major emission source regions of France and Spain. The emission estimates used in this scenario support concentrations as high as 23 pg m^{-3} with an estimated spatial variability of up to 2 orders of magnitude. Fig. 6a also presents relatively high concentrations towards the Central and Northeast Europe, an observation that agrees with the calculated wind roses and the predominant West-North West wind direction in Europe. The lowest concentrations are found in Southeast and Northwest Europe. These findings suggest that the current model description of the atmospheric transport of POPs produces realistic results and can provide the basis for further testing scenarios.

A slightly different pattern emerges in the case of the soil concentration/distribution (Fig. 6b). In this case, lindane is transported through air and water and is mainly deposited in the immediate vicinity of the major emission regions. High concentrations are, therefore, found in soils west and east of France. Another feature in Fig. 6b is the increased concentrations (through atmospheric deposition) in Scandinavian and other Northern European soils. This is attributed to the organic-rich terrestrial surfaces underlying these heavily

forested regions that have a high capacity for sorption of mainly gaseous-phase POPs from the atmosphere. Previous studies (McLachlan and Horstmann, 1998; Wania and McLachlan, 2001) have also highlighted the influence of forests on increasing the net atmospheric deposition to the terrestrial environment. The lowest soil concentrations are, again, found in the South and East. A factor of 100 difference in soil concentrations was evident, with a maximum of 15 pg g^{-1} in the grid representing Belgium, the Netherlands and Northeast France. Since no background concentrations or historical release trends were taken into account, the actual concentration values for all compartments are likely to be underestimated.

A mean value of 50 pg m^{-3} was used as an initial/background air concentration throughout Europe in order to reduce the spatial variability and compare model predicted concentrations to measured data. The model predictions using the background concentration data are shown in Fig. 7. The results show rapid “depletion” of the concentrations with distance from source due to the advection, degradation and other processes together with an average factor of 5 underestimation of air concentrations. This would suggest that either one (or both) of the following may be occurring:

- (a) The selected initial concentration is too small to support the measured ambient air levels, or/and
- (b) The source term is underestimated, for example, diffusive sources are not currently considered.

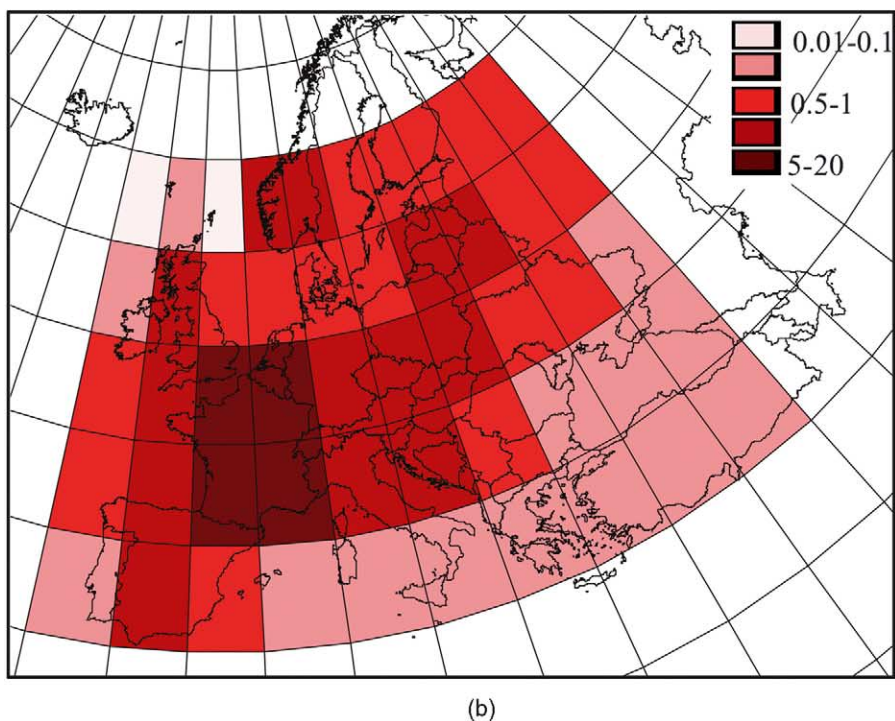
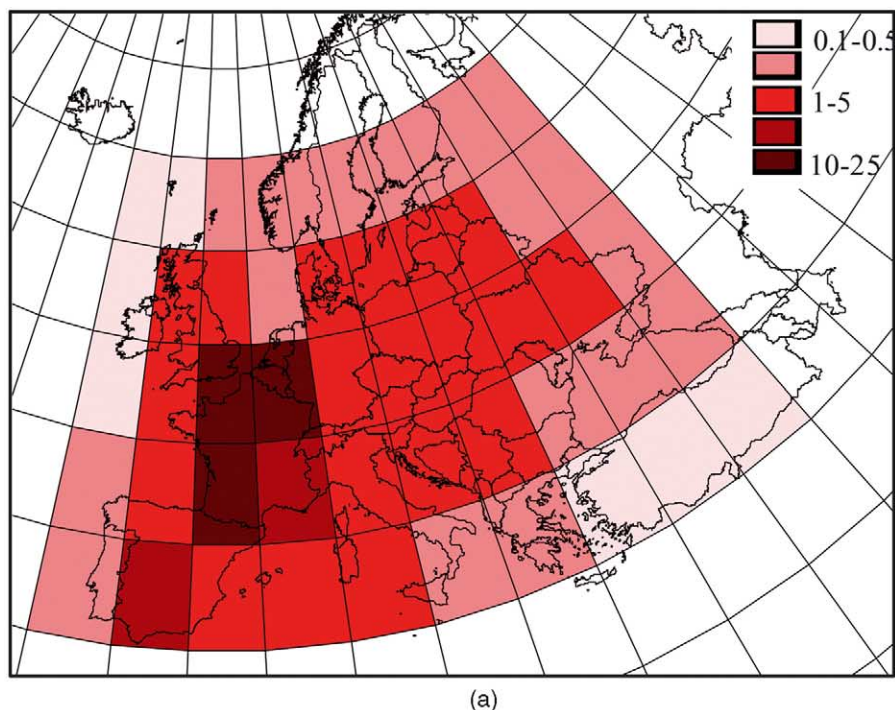


Fig. 6. (a) Lower air distribution (pg m^{-3}) (b) soil distribution (pg g^{-1}).

The output also reveals a similar picture to Fig. 6a, with the possible exception of higher concentrations towards the east. A greater influence from the local emission sources, together with the selected background value of 50 pg m^{-3} which sustains elevated ambient air levels, are the main reasons for these trends. They are also responsible for the much smaller spatial variability, which reduces to one order of magnitude ($2.6\text{--}26 \text{ pg}$

m^{-3}). This finding supports the well-documented transport potential of $\gamma\text{-HCH}$ (Beyer et al., 2003). Table 2 presents the predicted lower air concentrations for selected “inner” European model regions, geographically relevant measurement data for 1998 and the location of the station and its reference. In general measured and predicted concentrations fall within one order of magnitude at most sites.

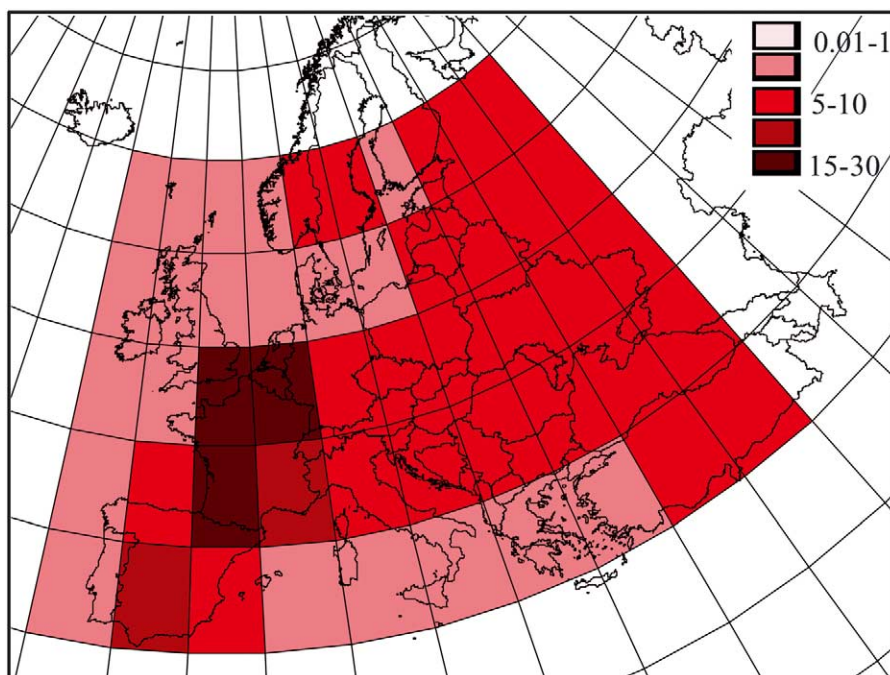


Fig. 7. Lindane lower air concentration with background (pg m^{-3}).

Table 2
Predicted and measured lower air concentrations

Region no.	Region	Lower air (pg/m^3)	Measured (pg/m^3)	Reference
4	W Norway	3.88	60; 6.7	UNEP, 2002; Lakaschus et al., 2002
6	E Sweden	5.01	25	Brorström-Lundén ^a
7	W Finland	4.79	10.4	Brorström-Lundén ^a
16	Denmark	4.94	25; 69, 11	UNEP, 2002; Lakaschus et al., 2002
19	Scotland	4.32	30	Lakaschus et al., 2002
26	Poland Ch	6.57	57	Holoubek ^a
39	N Spain	6.23	5.8	Lakaschus et al., 2002
41	S Portugal	4.00	7	Lakaschus et al., 2002
51	Arctic	5.12	8; 4.9	UNEP, 2002; Lakaschus et al., 2002

^a Personal communication.

Van Jaarsveld et al. (1997) have also modelled the atmospheric transport and deposition of lindane on a European scale, using a Lagrangian-type model and emission inventories for 1990. Their results are very similar to the model output presented here, with an underestimation of atmospheric lindane steady-state concentrations. They concluded that the under prediction was likely to have resulted from inaccuracies in the emission inventory. High deposition of lindane to sea bodies emphasised the role of seas as buffers for lindane, whilst re-emission to the atmosphere only appeared to occur under very low ambient atmospheric concentrations. The transport potential of lindane outside the continent was also highlighted. LRAT is predicted to be of primary importance following the predominant wind direction i.e. West–East. According to the model results, the Arctic is likely to be the recipient of long-range lin-

dane transport primarily via oceanic transport. Atmospheric concentrations of lindane in the “Arctic Box” air are relatively low, suggesting that the transport potential via the atmosphere from continental Europe is likely to be minimal. Modelling the global fate of α -HCH, Wania and Mackay (1999) also highlighted the small advective inflow into the Arctic environment via atmospheric transport.

6. Future model improvements and concluding remarks

A linked European scale multimedia model has been developed which describes the fate and behaviour of POPs under steady-state or dynamic conditions. Results for a steady-state solution for lindane have been presented which illustrate the apparent success of the re-

parameterisation process. Future efforts will be directed towards dynamic runs, utilising fully dynamic emission patterns. It is anticipated that future improvements of the model include in a more sophisticated parameterisation of the vegetation compartment and further investigations into model parameter sensitivity. The model is intended to provide a more environmentally realistic representation of fate and behaviour of POP chemicals within Europe with particular emphasis on transport processes. Models such as these can provide useful information identifying key processes and potential sinks, predictions of long-range transport and ultimately aid policy decisions by providing information on the potential impact of proposed source reduction strategies.

Acknowledgements

We wish to thank Professor Donald Mackay and the Canadian Environmental Modelling Centre for their invaluable help and hospitality. The authors also wish to acknowledge the assistance provided by Sam Pepler of the British Atmospheric Data Centre, Dr Duncan Whyatt of Lancaster University and DEFRA Air Quality Division Funding No. EPG 1/3/169.

References

- Breivik, K., Pacyna, J.M., Münch, J., 1999. Use of α -, β - and γ -hexachlorocyclohexane in Europe, in 1970–1996. *Science of the Total Environment* 239, 151–163.
- Bennett, D.H., McKone, T.E., Matthies, M., Kastenberger, W.E., 1998. General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment. *Environmental Science and Technology* 32, 4023–4030.
- Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E., 2000. Assessing long-range transport of persistent organic pollutants. *Environmental Science and Technology* 34, 699–703.
- Beyer, A., Wania, F., Gouin, T., Mackay, D., Matthies, M., 2003. Temperature dependence of the characteristic travel distance. *Environmental Science and Technology* 37, 766–771.
- Cousins, I.T., Mackay, D., 2001. Strategies for including vegetation compartments in multimedia models. *Chemosphere* 44, 643–654.
- Fellin, P., Barrie, L.A., Dougherty, D., Toom, D., Muir, D., Grift, N., Lockhart, L., Billeck, B., 1996. Air monitoring in the arctic: results for selected organic pollutants for 1992. *Environmental Toxicology and Chemistry* 15, 253–261.
- Hansen, D.V., Poulain, P.M., 1996. Quality control and interpolations of WOCE-TOGA drifter data. *Journal of Atmospheric and Oceanic Technology* 13, 900–909.
- Lakaschus, S., Weber, K., Wania, F., Bruhn, R., Schrems, O., 2002. The air-sea equilibrium and time trend of Hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica. *Environmental Science and Technology* 36, 138–145.
- Leemans, R., Cramer, W., 1991. The IIASA database for mean monthly values of temperature, precipitation and cloudiness of a global terrestrial grid. International Institute for Applied Systems Analysis (IIASA). RR-91-18.
- Li, Y.F., Bidleman, T.F., Barrie, L.A., McConnell, L.L., 1998. Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment. *Geophysical Research Letters* 25 (1), 39–41.
- MacLeod, M., Woodfine, D.G., Mackay, D., McKone, T., Bennet, D., Maddalena, R., 2001. BETR North America: a regionally segmented multimedia contaminant fate model for North America. *Environmental Science and Pollution Research* 8 (3), 156–163.
- Manz, M., Wenzel, K.D., Dietze, U., Schüumann, G., 2001. Persistent organic pollutants in agricultural soils in central Germany. *The Science of the Total Environment* 277 (1–3), 187–198.
- McLachlan, M.S., Horstmann, M., 1998. Forests as filters of airborne organic pollutants: a model. *Environmental Science and Technology* 32, 413–420.
- MTEC Technologie, 2000. Gaussian Algorithm (Elimination Method). Nurnberg, Germany. Available from <<http://ourworld.compuserve.com/homepages/MTEC/>>.
- Scheringer, M., Wegmann, F., Fenner, K., Hungerbühler, K., 2000. Investigation of the cold condensation of persistent organic pollutants with a global multimedia fate model. *Environmental Science and Technology* 34, 1842–1850.
- Smith, W.H.F., Sandwell, D.T., 1997. Global seafloor topography from satellite altimetry and ship depth soundings. *Science* 277, 1956–1962.
- United Nations Environment Programme (UNEP), 2002. Europe regional report: Regionally based assessment of Persistent Toxic substances.
- Van de Meent, D., 1993. SIMPLEBOX—A Generic Multimedia Fate Evaluation Model Report No. 672720001. National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands.
- Van Jaarsveld, J.A., Van Pul, W.A.J., De Leeuw, F.A.A.M., 1997. Modelling transport and deposition of persistent organic pollutants in the European region. *Atmospheric Environment* 31 (7), 1011–1024.
- Vorosmarty, C.J., Fekete, B.M., Tucker, B.A., 1998. Global River Discharge Database (RivDis), v. 1.1. Available from <http://www-eosdis.ornl.gov>.
- Wania, F., Mackay, D., 1995. A global distribution model for persistent organic chemicals. *The Science of the Total Environment* 160/161, 211–232.
- Wania, F., Mackay, D., 1999. Global chemical fate of α -hexachlorocyclohexane. 2. Use of a global distribution model for mass balancing, source apportionment, and trend prediction. *Environmental Toxicology and Chemistry* 18 (7), 1400–1407.
- Wania, F., McLachlan, M.S., 2001. Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multimedia fate model. *Environmental Science and Technology* 35, 582–590.
- Woodfine, D., MacLeod, M., Mackay, D., Brimacombe, J.R., 2001. Development of continental scale multimedia contaminant fate models: integrating GIS. *Environmental Science and Pollution Research* 8 (3), 164–172.